

FORM PCT 1390  
REV. 5/93

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NO.

VORTKORT ET AL-1 PCT

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

09/913613

INTERNATIONAL APPLICATION NO.  
PCT/DE00/00329INTERNATIONAL FILING DATE  
3 FEBRUARY 2000PRIORITY DATE CLAIMED  
15 FEBRUARY 1999

TITLE OF INVENTION

THERMOPLASTIC VULCANIZATE AND ITS METHOD OF PRODUCTION

APPLICANT(S) FOR DO/EO/US

JÖRG VORTKORT ET AL

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371 (f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau)
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has **NOT** expired.
  - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.  
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

PCT/ISA/210 - Int'l. Search Report (English)

Applicant Claims Priority under 35 U.S.C. §119 of GERMAN Application No. 199 06 002.9, filed 15 FEBRUARY 1999.  
 Applicant Claims Priority under 35 U.S.C. §120 of: PCT No. PCT/DE00/00329, filed 3 FEBRUARY 2000.

APPLICATION NO. (if known, see 37 CFR 1.5)

09/913613

INTERNATIONAL APPLICATION NO  
PCT/DE00/00329ATTORNEY'S DOCKET NO  
VORTKORT ET AL I PCT☒ The following fees are submitted:**Basic National Fee (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO.....\$860.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)  
.....\$690.00Neither international preliminary examination fee paid (37 CFR 1.82) nor  
international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....\$1,000.00International preliminary examination fee paid to USPTO (37 CFR 1.482)  
and all claims satisfied provisions of PCT Article 33(2)-(4).....\$100**ENTER APPROPRIATE BASIC FEE AMOUNT =**Surcharge of **\$130.00** for furnishing the oath or declaration later than \_\_\_\_ 20 \_\_\_\_ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

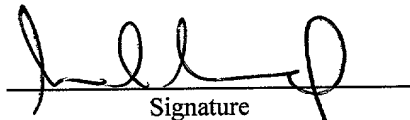
Claims	Number Filed	Number Extra	Rate		
Total Claims	18 - 20 =	- 0 -	X \$18.00	\$ 860.00	
Independent Claims	1 - 3 =	- 0 -	X \$80.00	\$	
Multiple dependent claim(s) (if applicable)			+ \$270.00	\$	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$ 860.00	
Reduction by 1/2 for Small Entity status, if applicable.				\$	
<b>SUBTOTAL =</b>				\$ 860.00	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
<b>TOTAL NATIONAL FEE =</b>				\$ 860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property +				See cover sheet attached to assign \$ to be charged to Deposit Acct	
<b>TOTAL FEES ENCLOSED =</b>				\$ 860.00	
				Amount to be: refunded	\$
				charged	\$

- a. ☒ A check in the amount of \$ 860.00 to cover the above fees is enclosed.
- b. \_\_\_\_ Please charge my Deposit Account No. 03-2468 in the amount of \$ \_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment, to Deposit Account No. 03-2468. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

COLLARD & ROE, P.C.  
1077 Northern Boulevard  
Roslyn, New York 11576-1696  
(516) 365-9802



Signature

Edward R. Freedman

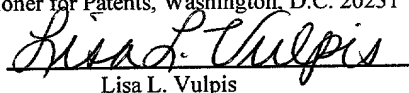
Reg. No. 26,048

Allison C. Collard

Reg. No. 22,532

Express Mail No. **EL 871 446 963 US**Date of Deposit **August 15, 2001**

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, on the date indicated above, and is addressed to the Ass't. Commissioner for Patents, Washington, D.C. 20231



Lisa L. Vulpis

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: JÖRG VORTKORT ET AL-1 PCT  
PCT NO.: PCT/DE00/00329 PCT FILED: 3 FEBRUARY 2000  
PRIORITY: 199 06 002.9 PRIORITY FILED: 15 FEBRUARY 1999  
TITLE: THERMOPLASTIC VULCANIZATE AND ITS METHOD OF PRODUCTION

PRELIMINARY AMENDMENT

**ATTN.: BOX PCT APPLICATION**

Ass't. Commissioner for Patents  
Washington, D.C. 20231

Dear Sir:

Preliminary to the initial Office Action, please amend the  
above-identified application as follows:

**IN THE SPECIFICATION:**

On Page 1, line 1, please insert the following paragraphs:

--CROSS REFERENCE TO RELATED APPLICATIONS

Applicants claim priority under 35 U.S.C. §119 of German  
Application No. 199 06 002.9, filed on 15 February 1999. Applicants  
also claim priority under 35 U.S.C. §120 of PCT/DE00/00329, filed  
on 3 February 2000. The international application under PCT  
article 21(2) was not published in English.--

On page 5, after line 1, please insert the following paragraph:

--Finally, it is pointed to EP A 0 092 318 which shows a thermoplastic blend of polyolefin and an elastomeric softener. The main objective is to be able to produce polypropylene foils of high value on polyethylene-working machines.--

On page 5, please substitute the second complete paragraph with the following paragraph:

--Said problem is solved by a thermoplastic vulcanizate comprised of a composition according to claim<sup>21</sup>, whereby useful material parameters are specified in claims 22 to 27.--

On page 5, please substitute the fourth complete paragraph with the following paragraph:

--In said conjunction, claims 28 to 38 contain useful process steps.--

On page 7, please substitute the first complete paragraph with the following paragraph:

--The component of the non-cross-linked polyethylene amounts

to from 5 to 25% by weight and from 5 to 15% by weight,  
respectively, again based on the sum of the four components (A, B,  
C, D).--

On page 7, please substitute the last complete paragraph with  
the following paragraph:

--The at least partially vulcanized rubber (C) has a degree of  
cross-linking of > 90%, in particular > 95%. A method for the  
determination of the degree of cross-linking is described in patent  
US-A-4,311,268.--

On page 8, please substitute the third complete paragraph with  
the following paragraph:

--The quantitative proportion of the plasticizer component  
amounts to from 25 to 40% by weight or from 25 to 50% by weight,  
respectively, again based on the sum of the four components (A, B,  
C, D).--

A marked-up copy of the prior pending paragraphs showing the  
changes made, is attached hereto.

**IN THE ABSTRACT:**

Please add the attached Abstract of the Disclosure on a separate page.

**IN THE CLAIMS:**

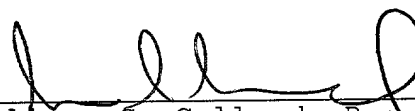
Please cancel claims 1-20 and replace with new claims 21-38 as attached hereto.

**REMARKS**

By this Preliminary Amendment, the application has been amended to conform with U.S. practice, the cross-reference to the related application has been inserted on page 1. Also, claims 1-20 have been replaced by new claims 21-38. In addition, an Abstract of the Disclosure has been added on its own separate. No new matter has been introduced.

Entry of this amendment is respectfully requested.

Respectfully submitted,  
JÖRG VORTKORT ET AL-1 PCT



COLLARD & ROE, P.C.  
1077 Northern Boulevard  
Roslyn, New York 11576  
(516) 365-9802

Allison C. Collard, Reg. No. 22,532  
Edward R. Freedman, Reg. No. 26,048  
Attorneys for Applicants

Express Mail No. EL 871 446 963 US  
Date of Deposit August 15, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. § 1.10, on the date indicated above, and is addressed to the Ass't. Commissioner for Patents, Washington, D.C. 20231

  
Lisa L. Vulpis

21. A thermoplastic vulcanizate comprised of four components (A, B, C, D), notably

- a thermoplastic synthetic resin (A);
- a substantially non-cross-linked polyethylene (B);
- a rubber (C) having a degree of cross-linking of  $> 90\%$  and being compatible with the thermoplastic synthetic resin (A) in regard to the phase inversion; and
- a plasticizer (D);

as well as of the standard blend ingredients (E) comprising at least one cross-linking agent or cross-linking system, whereby the mixture is comprised of the following quantitative proportions (in % by weight) based on the sum of the four components (A, B, C, D):

- |                                     |                       |
|-------------------------------------|-----------------------|
| - Thermoplastic synthetic resin (A) | 5 to 20               |
| - Polyethylene (B)                  | 25 to 5 or 15 to 5    |
| - Rubber (C)                        | 30 to 50              |
| - Plasticizer (D)                   | 40 to 25 or 50 to 25. |

22. The thermoplastic vulcanizate according to claim 21, characterized in that the standard ingredients (E) of the blend are added in from 0.02 to 0.5 times the amount by weight based on the sum of the four components (A, B, C, D).

23. The thermoplastic vulcanizate according to claim 21, characterized in that the thermoplastic synthetic resin (A) is a polypropylene based on a homopolymer, block polymer or copolymer preferably in conjunction with high crystallinity.

24. The thermoplastic vulcanizate according to claim 21, characterized in that the polyethylene (B) is a VLDPE with a density of from 0.88 to 0.91 g/cm<sup>3</sup> at 20°C and/or a ULDPE with a density of from 0.85 to 0.88 g/cm<sup>3</sup> at 20°C.

25. The thermoplastic vulcanizate according to claim 21, characterized in that the rubber (C) is an EPDM rubber, whereby the third monomer is preferably an ethylidene-norbornene.

26. The thermoplastic vulcanizate according to claim 21, characterized in that the rubber (C) has a degree of cross-linking of > 90%, preferably > 95%.

27. The thermoplastic vulcanizate according to claim 21, characterized in that the plasticizer (D) is a plasticizer oil, in particular a paraffinic oil with a component of aromatics of <4% by weight, preferably a paraffinic plasticizer oil free of



aromatics.

28. A method for producing a thermoplastic vulcanizate according to claim 21, characterized in that the rubber (C) in the still-unvulcanized state is first mixed with a plasticizer (D) and the standard blend ingredients (E) in a roll or screw extruder, whereby the standard blend ingredients preferably still not yet contain a cross-linking agent or cross-linking system.

29. The method for producing a thermoplastic vulcanizate according to claim 28, characterized by the following process steps:

- feeding of the unvulcanized rubber (C) and the standard blend ingredients (E);
- meltdown and dispersion of the rubber (C) as well as of the standard blend ingredients (E); and
- addition of the plasticizer (D) while mixing with the two charged components (C, E).

30. The method for producing a thermoplastic vulcanizate according to claim 28, characterized in that the plasticizer (D) and the standard blend ingredients (E) are admixed into the unvulcanized rubber (C) in the first third part of the roll or screw extruder.

31. The method for producing a thermoplastic vulcanizate

according to claim 28, characterized in that mixture comprised of the thermoplastic synthetic resin (A), and the non-cross-linked polyethylene (B) is added downstream of the first third part of the roll or screw extruder.

32. The method for producing a thermoplastic vulcanizate according to claim 21, characterized in that in a roll or screw extruder, the rubber (C) in the still-unvulcanized state is substantially simultaneously mixed with the thermoplastic synthetic resin (A), the non-cross-linked polyethylene (B), the plasticizer (D) and the standard blend ingredients (E), whereby the standard blend ingredients preferably not yet contain a cross-linking agent or cross-linking system.

33. The method for producing a thermoplastic vulcanizate according to claim 32, characterized in that the thermoplastic synthetic resin (A), the non-cross-linked polyethylene (B), the plasticizer (D) and the standard blend ingredients (E) are admixed into the unvulcanized rubber (C) in the first third part of the roll or screw extruder.

34. The method for producing a thermoplastic vulcanizate according to claim 28, characterized in that a non-cross-linked rubber (C) is used, said rubber being present in a flowable state, preferably in the form of a flowable pellet or granulate.

35. The method for producing a thermoplastic vulcanizate

according to claim 28, characterized in that following mixing of the four components (A, B, C, D) and the standard blend ingredients (E) without the cross-linking agent or cross-linking system, the cross-linking agent or the cross-linking system is now added in conjunction with the following steps of the process:

- Dynamic vulcanization of the rubber (C) at high shear and expansion rates;
- degassing of the dynamically vulcanized plastic melt, in particular under vacuum; and
- building up the pressure for ejecting the thermoplastic vulcanizate from the mold.

36. The method for producing a thermoplastic vulcanizate according to claim 35, characterized in that all steps of the method connected with the addition of the cross-linking agent or cross-linking system are carried out in the second half of the roll or screw extruder.

37. The method for producing a thermoplastic vulcanizate according to claim 28,

characterized in that a cross-linking agent or cross-linking system is used that cross-links the rubber (C) on the one hand, and prevents the polyethylene (B) from cross-linking on the other, preferably based on a phenolic resin, in particular again in connection with an accelerator consisting of tin dichloride.

38. The method for producing a thermoplastic vulcanizate according to claim 28, characterized in that the preparation of the mixture comprised of the four components (A, B, C, D) and all of the standard blend ingredients (E) is carried out in a single-stage process.

## **ABSTRACT**

The invention relates to a thermoplastic vulcanizate comprising four components (A, B, C, D), notably: a thermoplastic (A); a substantially non-cross-linked polyethylene (B); an at least partially vulcanized rubber (C); a softener (D); as well as standard blend ingredients (E). The above mixture contains between 5 and 20% by weight thermoplastic (A), in relation to the sum of the four components (A, B, C, D). The invention also relates to advantageous material parameters and process steps.

Marked-Up Version Showing Changes Made

On page 5, please substitute the second complete paragraph with the following paragraph:

--Said problem is solved [according to patent claim 1] by a thermoplastic vulcanizate comprised of a composition according to claim 21, [claim 1] whereby useful material parameters are specified in claims [2 to 9] 22 to 27.--

On page 5, please substitute the fourth complete paragraph with the following paragraph:

--In said conjunction, claims [10 to 20] 28 to 38 contain useful process steps.--

On page 7, please substitute the first complete paragraph with the following paragraph:

--The component of the non-cross-linked polyethylene [usefully] amounts to from 5 to 25% by weight and from 5 to 15% by weight, respectively, again based on the sum of the four components (A, B, C, D).--

On page 7, please substitute the last complete paragraph with the following paragraph:

--The at least partially vulcanized rubber (C) [usefully] has a degree of cross-linking of  $> 90\%$ , in particular  $> 95\%$ . A method for the determination of the degree of cross-linking is described in patent US-A-4,311,628.--

On page 8, please substitute the third complete paragraph with the following paragraph:

--The quantitative proportion of the plasticizer component [preferably] amounts to from 25 to 40% by weight or from 25 to 50% by weight, respectively, again based on the sum of the four components (A, B, C, D).--

THERMOPLASTIC VULCANIZATE AND ITS METHOD OF PRODUCTION

## Description

The invention relates to a thermoplastic vulcanizate.

Thermoplastic vulcanizates are blends that are comprised of a thermoplastic and a cross-linked elastomer. The process of cross-linking of the elastomer is carried out by dynamic vulcanization. The term "dynamic vulcanization" is understood to relate to a process in which the thermoplastic material, the rubber and the cross-linking system are masticated while the rubber is being cross-linked. Examples of dynamic vulcanization are described in the patents US-A 4,130,535 and US-A 4,311,628. Laid-open patent specification DE-A 26 32 654 describes a blend that is comprised of a thermoplastic polyolefin, an EPDM rubber and any one of the cross-linking systems known from US-A 3,806,558. The rubber is vulcanized to such a degree that that it no longer contains more than about three percent of rubber that can be extracted in cyclohexane at 23°C. GB-A 2 007 683 describes a thermoplastic elastomer containing a thermoplastic, crystalline polyolefin resin and vulcanized EPDM. The rubber is cross-linked in a phenolic resin. The degree of cross-linking so achieved is higher than 97%. Furthermore, WO-A 98/58020 describes a TPE blend based on a thermoplastic olefin, an EPDM



particularly important for the further advance of TPE materials in the field of application of the classical elastomers. Soft thermoplastic vulcanizates are understood in the following to be materials with a hardness of less than 70 Shore A (said value relates to measurements on extruded flat sections). Since the absorption of oil of the rubber phase is limited, minimum hardness values of about 50 Shore A can be obtained in connection with thermoplastic vulcanizates based on EPDM/PP by adding plasticizer oils (EP-A 0 757 077). Even in said hardness range, the increasing amount of the oil component already leads to a decrease in the mechanical properties as well as to increased fogging values. Also, it may be possible that the oil sweats out on the surface of the molded component. The values specified herein in the following are given only by way of example. Based on 100 parts rubber, a thermoplastic vulcanizate with a hardness of 50 Shore A contains about 150 to 200 parts of oil. In order to keep the technical processing expenditure within economically justifiable limits when the plasticizer oil is mixed in, EPDM rubbers extended with oil are preferably used. Again, however, a drawback is also in this connection the fact that the EPDM-types of rubber extended with oil are expensive in comparison to the non-diluted types of EPDM. Furthermore, types of EPDM extended with oil are available in the market, which are extended with 75 or 100 parts and contain plasticizer oils that comprise aromatics, so that discoloration

occurs during in the course of wheathering. Therefore, the production of bright and soft thermoplastic vulcanizates poses special problems. With the dynamic vulcanizates available in the market on the basis of EPDM/PP, discoloration can be restricted only by means of suitably high expenditure on the raw material side, but is not entirely avoidable.

The addition of styrene block copolymers, which leads to a reduction in the hardness as well, is expensive and, furthermore, reduces the weather stability.

The patent literature cited in the following introduces formulas and process variations that permit the production of thermoplastic vulcanizates. A very soft thermoplastic vulcanizate (< 60 Shore A, preferably < 45 Shore A) is described in EP-A 0 757 077. Said vulcanizate consists of two vulcanized rubbers EPDM and BR, or SBR or CR, and a larger amount of process oil. The vulvanized rubbers are present in the thermoplastic matrix in the form of a finely distributed dispersed phase. A soft thermoplastic vulcanizate with a partially cross-linked rubber phase is introduced in WO-A 97/39059, which preferably consists of a thermoplastic polyethylene (homo- or copolymer), an amorphous polypropylene, and an EPDM- or BR-rubber. The amorphous polypropylene is preferably added only after the rubber has been dynamically

vulcanized.

Now, as the thermoplastic vulcanizates known until now are afflicted with the drawbacks of higher technical processing expenditure and/or connected with high costs, the invention is based on the problem of developing a more favorably priced, soft thermoplastic vulcanizate that exhibits an only minor tendency to discoloration in the course of weathering.

Said problem is solved according to patent claim 1 by a thermoplastic vulcanizate comprised of a composition according to claim 1, whereby useful material parameters are specified in claims 2 to 9.

Furthermore, the problem of the invention consists in producing the thermoplastic vulcanizate as defined by the invention without increased expenditure in terms of process technology.

In said conjunction, claims 10 to 20 contain useful process steps.

The thermoplastic vulcanizate and the method for producing it as defined by the invention are now described in the following in greater detail.

According to claim 1, the thermoplastic vulcanizate is comprised of four components (A, B, C, D), notably

- a thermoplastic (A);
- a substantially non-cross-linked polyethylene (B);
- an at least partially vulcanized rubber (C); and
- a plasticizer (D);

as well as the standard ingredients (E) of the blend, whereby the individual groups of materials are now introduced in the following in greater detail.

#### Thermoplastic (A)

It is possible to use any desired thermoplastics such as, for example polystyrene, polyamide, polyester or polypropylene in the form of plastic mixtures, among others. The plastic preferably employed is a polypropylene based on a homopolymer, or on block polymers or copolymers, preferably again in association with high crystallinity.

The component of the thermoplastic amounts to 5 to 20% by weight notably based on the sum of the four components (A, B, C, D).

#### Non-cross-linked polyethylene (B)

The substantially non-cross-linked polyethylene is preferably a VLDPE (= very low density polyethylene) with a

density of 0.88 to 0.91 g/cm<sup>3</sup> at 20°C and/or a ULDPE (= ultra low density polyethylene) with a density of 0.85 to 0.88 g/cm<sup>3</sup> at 20°C.

The component of the non-cross-linked polyethylene usefully amounts to from 5 to 25% by weight and from 5 to 15% by weight, respectively, again based on the sum of the four components (A, B, C, D).

#### Vulcanized rubber (C)

Various types of rubber can be employed such as, for example types based on natural rubber (NR), butyl rubber (BR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), or an ethylene-propylene-diene copolymer (EPDM), whereby attention has to be paid to its compatibility with the thermoplastic (A) particularly with respect to the phase inversion.

The rubber employed is preferably an EPDM rubber. The third monomer may be hexadiene-1,4, dicyclopentadiene, or in particular ethylidene-norbornene.

The at least partially vulcanized rubber (C) usefully has a degree of cross-linking of > 90%, in particular > 95%. A method for the determination of the degree of cross-linking is described in patent US-A-4,311,628.

The preferred quantitative proportion of the rubber component amounts to from 30 to 50% by weight notably based on the sum of the four components (A, B, C, D).

#### Plasticizer (D)

Any desired suitable plasticizer can be employed for extending the rubber. In particular paraffinic or naphthalic oils are used for extending the EPDM rubber. The plasticizer oil in the present connection is usefully a paraffinic oil with an aromatic component of < 4% by weight notably based on the total mass of the plasticizer. However, particularly a paraffinic plasticizer oil that is free of aromatics is employed.

The quantitative proportion of the plasticizer component preferably amounts to from 25 to 40% by weight or from 25 to 50% by weight, respectively, again based on the sum of the four components (A, B, C, D).

#### Standard ingredients of the blend (E)

An important component is the cross-linking agent or the cross-linking system that additionally contains cross-linking aids (e.g. accelerators). A cross-linking agent or cross-linking system based on a phenolic resin is preferably used, in

particular in association with an accelerator consisting of tin dichloride. In this way, a high degree of cross-linking of the rubber (C) is obtained on the one hand, and the polyethylene (B) is prevented from cross-linking on the other.

Furthermore, in most cases, the standard ingredients of the blend comprise a filler as well as additives, whereby the following additives need to be mentioned by way of example: anti-aging agents, UV-absorbers, dye pigments, flame-retarding agents, fluxing agents and/or auxiliary processing agents.

The standard ingredients of the blend are usefully added in from 0.02 to 0.5 times the amount by weight, notably based on the sum of the four components (A, B, C, D).

Now, the preferred steps of the method for producing the thermoplastic vulcanizate as defined by the invention are described in the following, notably in the form of two variations (u, v):

#### Variation (u)

- The still-unvulcanized rubber (C) and the standard blend ingredients (E) are first admitted into a continuously operating roll or screw extruder without the cross-linking agent or cross-linking system. The non-cross-linked rubber

is present in this connection in a flowable state,  
preferably in the form of flowable pellets or a granulate.

- The unvulcanized rubber (C) as well as the standard blend ingredients (E) are now melted down and dispersed.
- The plasticizer (D) is subsequently added and admixed with the two charged components (C, E).
- The plasticizer (D) and the standard blend ingredients (E) are preferably added in this process to the unvulcanized rubber (C) within the first third part of the roll or screw extruder.
- The mixture comprising the thermoplastic (A) and the non-cross-linked polyethylene (B) is now added, whereby said mixture is particularly added downstream of the first third part of the roll or screw extruder. Meltdown and dispersion of the components (A, B) occur in this step combined with homogenization of the melt.
- Thereafter, the cross-linking agent or the cross-linking system is added, whereby the dynamic vulcanization of the rubber (C) takes place at high shearing and expansion rates,



which amount to at least  $100 \text{ s}^{-1}$ , in particular 500 to 1500  $\text{s}^{-1}$ . Furthermore, degassing of the dynamically vulcanized plastic melt, in particular under vacuum, and the subsequent pressure build-up for ejecting the thermoplastic vulcanizate from the mold are associated with the present step of the method. The entire step of the method described above preferably takes place in the second half of the roll or screw extruder.

- Finally, the thermoplastic vulcanizate ejected from the mold is usually granulated following cooling.

#### Variation (v)

According to another variation, the rubber (C) in the still-unvulcanized state is substantially simultaneously mixed with the thermoplastic (A), the non-cross-linked polyethylene (B), the plasticizer (D) and the standard blend ingredients (E) in a roll or screw extruder; however, without the cross-linking agent or cross-linking system. In the present case, too, admixing preferably takes place in the first third part of the roll or screw extruder.

Reference is made to variation (u) with respect to the addition of the cross-linking agent or cross-linking system and

the dynamic vulcanization, as well as in regard to the subsequent steps.

The preparation of the mixture of the four components (A, B, C, D) and of all of the standard blend ingredients (E) of the mixture takes place in a single-stage process irrespective of which of the two variations (u, v) is involved.

The thermoplastic vulcanizate and the method as defined by the invention are described in the following by way of example with the help of experimental data.

A Berstorff twin-screw extruder ZE 25 with a length of 54 D and equipped with screws rotating in the same sense was employed as the test production line. The maximally possible number of revolutions of the screws amounts to 500 min<sup>-1</sup>. The EPDM-pellets (A) and the standard blend ingredients (E) of the mixture including the tin dichloride as the accelerator, however, without the cross-linking agent, are metered into the feed opening of the extruder. After the rubber phase is melted down, the plasticizer (D) is injected and admixed in the first third part of the extruder. The mixture comprised of the polypropylene (A) and the polyethylene (B) is added farther downstream. Following meltdown and homogenization of the plastic melt, the phenolic resin is added. Within the framework

of a technological processing alternative it is possible also at this point to add in a metered manner a cross-linking system which, in the present case, is comprised of the phenolic resin and the tin dichloride. The dynamic vulcanization of the rubber phase, the degassing of the melt and the pressure build-up for ejecting the vulcanizate from the mold take place in the second half of the extruder. The strand of compound is cooled in a water basin and subsequently granulated.

The granulate is dried for 3 hours at 80°C and subsequently processed to test specimens on an injection molding machine.

Table 1 shows a summary of a number of mixing formulas by way of example. Furthermore, table 2 represents a few material data of the reference mixtures and the mixtures as defined by the invention. With respect to the measured Shore hardness values it has to be noted that based on past experience, the hardness values determined on an injection-molded test specimens exceed the values measured on extruded flat sections by 3 to 5 points. Mixture I represents the starting basis of the tests. The mixture extended with 100 parts paraffinic plasticizer oil and without VLDPE has a hardness of 70 Shore A. The reference mixtures II and III were adjusted softer by adding additional paraffinic oil. Because of the high oil component of said mixtures it was necessary to produce said

mixtures in a two-stage process. The hardness of the reference mixture II extended with 125 parts oil amounts to 65 Shore A, and of the reference mixture III with 150 parts oil comes to 62 Shore A. The mixtures IV and V as defined by the invention were extended with 100 parts oil. In the mixtures IV and V as defined by the invention, VLDPE was substituted for a portion of the polypropylene, as compared to the mixtures I to III. The mixtures IV and V are softer by 10 and, respectively, 13 Shore A versus the mixture I while containing the same proportion of oil. The strength of the mixture V as defined by the invention is comparable to the value of the harder mixture II. In mixture IV, the proportion of the thermoplastic phase was increased from 50 to 60 parts. It was possible in this way to increase the process safety in the production of the thermoplastic vulcanizate without permitting the hardness of the mixture to substantially increase. The hardness of said mixture IV as defined by the invention comes to 10 Shore below the value of the mixture I. The tensile values and the values of deformation under pressure of the mixtures IV and V as defined by the invention are comparable or superior to those obtained with the reference mixtures I to III.

The thermoplastic vulcanizate as defined by the invention exhibits a pleasant haptics similar to rubber. The strength values exceed the level of vulcanizates with equal hardness,

excluding thermoplastic vulcanizates extended with oil. By partly substituting non-cross-linked polyethylene (B) for the plasticizer (D) and reducing at the same time the polypropylene component (A), it is possible to produce also soft thermoplastic vulcanizates at favorable cost in a single-stage process, using a roll or screw extruder system. Particularly owing to the use of a non-extended, flowable EPDM, again in particular in connection with a plasticizer oil that is free of aromatics, it is possible to produce soft and bright, weather-resistant thermoplastic vulcanizates.

Furthermore, the tests carried out have shown that the novel type of thermoplastic vulcanizate offers substantial benefits with respect to process safety as well.

The morphological conversion from the phase-phase morphology (non-cross-linked rubber - thermoplastic resin) into the morphology of the particle matrix (vulcanized rubber - thermoplastic resin) is determined in the course of the dynamic vulcanization by the viscosity ratio and the mass ratio of the rubber phase to the thermoplastic phase. Especially in connection with the soft thermoplastic vulcanizates, the morphological conversion during the dynamic vulcanization becomes increasingly more difficult because of the low proportion of the thermoplastic component. By adding

polyethylene (B) and reducing at the same time the polypropylene component (A), it is possible to produce a softer thermoplastic vulcanizate while the process safety remains constantly high. As the polyethylene (B) is present in a substantially non-cross-linked state, the thermoplastic vulcanizate as defined by the invention exhibits good flowability.

Table 1

FORMULA	I pbw	II pbw	III pbw	IV pbw	%	V pbw	%
A Polypropylene	50	50	50	35	13.46	30	12
B VLDPE	-	-	-	25	9.62	20	8
C EPDM rubber	100	100	100	100	38.46	100	40
D Plasticizer	100	125	150	100	38.46	100	40
E Fillers and additives	36	36	36	36		36	
Tin chloride	1	1	1	1		1	
Phenolic resin	6	6	6	6		6	
Sum	293	318	343	303		293	

Pbw = parts by weight

% = percent by weight

Raw materials used:

EPDM rubbers : Royalene IM 7100 / Buna EPG 6470C

Polypropylene: Eltex P HF 100 / Moplen Q 30 P

VLDPE : Clearflex MQFO / Clearflex MPDO

Plasticizer : Tudalen 9246/ Enerpar M 1930

Filler : Barytmehl N 903 / Polestar 200 R

Additives : Irganox 1010 / Irganox 1135 / Tinuvin 770 /  
Chemisorb 944

Phenolic resin: SP 1045

Table 2:

Characteristics of mixtures I to V

Formula No.	I	II	III	IV	V
Hardness Shore A [Skt]	70	65	62	60	57
Tear resistance [N/mm <sup>2</sup> ]	4.3	3.3	2.8	3.4	3.2
Elongation at rupture [%]	233	229	209	180	196
DVR (25%/22h/RT) [%]	21	22	21	19	16
DVR (25%/22h/70°) [%]	33	34	35	37	31
DVR (25%/22h/100°C) [%]	44	41	44	40	33
ZVR (25%/22h/RT) [%]	-	23	22	22	18

## Claims

1. A thermoplastic vulcanizate comprising four components (A, B, C, D), specifically:

- a thermoplastic (A);
- a substantially non-cross-linked polyethylene (B);
- an at least partially vulcanized rubber (C); and
- a plasticizer (D);

as well as, furthermore, the standard blend ingredients (E), whereby the mixture contains from 5 to 20% by weight thermoplastic synthetic resin (A), notably based on the sum of the four components (A, B, C, D).

2. The thermoplastic vulcanizate according to claim 1, characterized in that the mixture comprises the following quantitative proportions with respect to the four components (A, B, C, D):

Thermoplastic synthetic resin (A)	5 to 20% by wt.
Polyethylene (B)	25 to 5% by wt.
Rubber (C)	30 to 50% by wt.
Plasticizer (D)	40 to 25% by wt.

3. The thermoplastic vulcanizate according to claim 1, characterized in that the mixture comprises the following



quantitative proportions with respect to the four components (A, B, C, D):

Thermoplastic synthetic resin (A)	5 to 20% by wt.
Polyethylene (B)	15 to 5% by wt.
Rubber (C)	30 to 50% by wt.
Plasticizer (D)	50 to 25% by wt.

4. The thermoplastic vulcanizate according to any one of claims 1 to 3, characterized in that the standard ingredients (E) of the blend are added in from 0.02 to 0.5 times the amount by weight based on the sum of the four components (A, B, C, D).

5. The thermoplastic vulcanizate according to any one of claims 1 to 4, characterized in that the thermoplastic synthetic resin (A) is a polypropylene based on a homopolymer, block polymer or copolymer preferably in conjunction with high crystallinity.

6. The thermoplastic vulcanizate according to any one of claims 1 to 5, characterized in that the polyethylene (B) is a VLDPE with a density of from 0.88 to 0.91 g/cm<sup>3</sup> at 20°C and/or a ULDPE with a density of from 0.85 to 0.88 g/cm<sup>3</sup> at 20°C.

7. The thermoplastic vulcanizate according to any one of claims 1 to 6, characterized in that the rubber (C) is an EPDM

rubber, whereby the third monomer is preferably an ethylidene-norbornene.

8. The thermoplastic vulcanizate according to any one of claims 1 to 7, characterized in that the rubber (C) has a degree of cross-linking of  $> 90\%$ , preferably  $> 95\%$ .

9. The thermoplastic vulcanizate according to any one of claims 1 to 8, characterized in that the plasticizer (D) is a plasticizer oil, in particular a paraffinic oil with a component of aromatics of  $< 4\%$  by weight, preferably a paraffinic plasticizer oil free of aromatics.

10. A method for producing a thermoplastic vulcanizate according to any one of claims 1 to 9, characterized in that the rubber (C) in the still-unvulcanized state is first mixed with a plasticizer (D) and the standard blend ingredients (E) in a roll or screw extruder, whereby the standard blend ingredients preferably still not yet contain a cross-linking agent or cross-linking system.

11. The method for producing a thermoplastic vulcanizate according to claim 10, characterized by the following process steps:

- feeding of the unvulcanized rubber (C) and the standard blend ingredients (E);
- meltdown and dispersion of the rubber (C) as well as of the standard blend ingredients (E); and
- addition of the plasticizer (D) while mixing with the two charged components (C, E).

12. The method for producing a thermoplastic vulcanizate according to claim 10 or 11, characterized in that the plasticizer (D) and the standard blend ingredients (E) are admixed into the unvulcanized rubber (C) in the first third part of the roll or screw extruder.

13. The method for producing a thermoplastic vulcanizate according to any one of claims 10 to 12, characterized in that mixture comprised of the thermoplastic synthetic resin (A), and the non-cross-linked polyethylene (B) is added downstream of the first third part of the roll or screw extruder.

14. The method for producing a thermoplastic vulcanizate according to any one of claims 1 to 9, characterized in that in a roll or screw extruder, the rubber (C) in the still-unvulcanized state is substantially simultaneously mixed with the thermoplastic synthetic resin (A), the non-cross-linked polyethylene (B), the plasticizer (D) and the standard blend

ingredients (E), whereby the standard blend ingredients preferably not yet contain a cross-linking agent or cross-linking system.

15. The method for producing a thermoplastic vulcanizate according to claim 14, characterized in that the thermoplastic synthetic resin (A), the non-cross-linked polyethylene (B), the plasticizer (D) and the standard blend ingredients (E) are admixed into the unvulcanized rubber (C) in the first third part of the roll or screw extruder.

16. The method for producing a thermoplastic vulcanizate according to any one of claims 10 to 15, characterized in that a non-cross-linked rubber (C) is used, said rubber being present in a flowable state, preferably in the form of a flowable pellet or granulate.

17. The method for producing a thermoplastic vulcanizate according to any one of claims 10 to 16, characterized in that following mixing of the four components (A, B, C, D) and the standard blend ingredients (E) without the cross-linking agent or cross-linking system, the cross-linking agent or the cross-linking system is now added in conjunction with the following steps of the process:

- Dynamic vulcanization of the rubber (C) at high shear and expansion rates;
- degassing of the dynamically vulcanized plastic melt, in particular under vacuum; and
- building up the pressure for ejecting the thermoplastic vulcanizate from the mold.

18. The method for producing a thermoplastic vulcanizate according to claim 17, characterized in that all steps of the method connected with the addition of the cross-linking agent or cross-linking system are carried out in the second half of the roll or screw extruder.

19. The method for producing a thermoplastic vulcanizate according to any one of claims 10 to 18, in particular in association with claim 17 or 18, characterized in that a cross-linking agent or cross-linking system is used that cross-links the rubber (C) on the one hand, and prevents the polyethylene (B) from cross-linking on the other, preferably based on a phenolic resin, in particular again in connection with an accelerator consisting of tin dichloride.

20. The method for producing a thermoplastic vulcanizate according to any one of claims 10 to 19, characterized in that the preparation of the mixture comprised of the four components

(A, B, C, D) and all of the standard blend ingredients (E) is carried out in a single-stage process.

R:\INGRID\DOCS\Vortkort et al PCT - Transl

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**THERMOPLASTIC VULCANIZATE AND ITS METHOD OF PRODUCTION**

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No. \_\_\_\_\_

on \_\_\_\_\_,

and was amended

on \_\_\_\_\_ (if applicable).

☒ was filed as PCT international application

Number PCT/DE00/00329

on 3 FEBRUARY 2000,

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

**PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:**

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. 119
GERMANY	199 06 002.9	15 FEBRUARY 1999	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**  
(Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER  
VORTKORT ET AL-1 PCT

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

**PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:**

U.S. APPLICATIONS			STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE		PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration numbers):  
KURT KELMAN, Registration No. 18,628  
ALLISON C. COLLARD, Registration No. 22,532  
EDWARD R. FREEDMAN, Registration No. 26,048  
ELIZABETH COLLARD RICHTER, Registration No. 35,103  
WILLIAM C. COLLARD, Registration No. 38,411  
FREDERICK J. DORCHAK, Registration No. 29,298  
REINE H. GLANZ, Registration No. 46,728

Send Correspondence to:

COLLARD & ROE, P.C.  
1077 Northern Boulevard  
Roslyn, New York 11576

Customer No. **25889**

Direct Telephone Calls to:  
(name and telephone number)  
**(516) 365-9802**

1-002	FULL NAME OF INVENTOR	FAMILY NAME <u>VORTKORT</u>	FIRST GIVEN NAME <u>JÖRG</u>	SECOND GIVEN NAME
	RESIDENCE & CITIZENSHIP	CITY <u>TOPPENSTEDT</u>	STATE OR FOREIGN COUNTRY <u>GERMANY</u>	COUNTRY OF CITIZENSHIP <u>GERMANY</u> <i>DEX</i>
	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>WULFSENER STRASSE 17</u>	CITY <u>D-21442 TOPPENSTEDT</u>	STATE & ZIP CODE/COUNTRY <u>GERMANY</u>
2002	FULL NAME OF INVENTOR	FAMILY NAME <u>GRÄBNER</u>	FIRST GIVEN NAME <u>FRIEDRICH</u>	SECOND GIVEN NAME <u>WILHELM</u>
	RESIDENCE & CITIZENSHIP	CITY <u>STELLE</u>	STATE OR FOREIGN COUNTRY <u>GERMANY</u>	COUNTRY OF CITIZENSHIP <u>GERMANY</u> <i>DEX</i>
	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>JAHNSTRASSE 8</u>	CITY <u>D-21435 STELLE</u>	STATE & ZIP CODE/COUNTRY <u>GERMANY</u>

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201

*J. V. A. K.*

SIGNATURE OF INVENTOR 202

*[Signature]*

DATE

*11.06.2007*

DATE

*11/12007*



COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Includes Reference to PCT International Applications)				ATTORNEY'S DOCKET NUMBER VORTKORT ET AL-1 PCT
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
		BONTEMPS	ANDRE	
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
		HAMBURG	GERMANY	GERMANY DEX
3	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
		TILEMANNHÖHE 14A	D-21079 HAMBURG	GERMANY
4	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
		VOLKMANN	STEFAN	
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
		ESCHEDE	GERMANY	GERMANY DEX
4	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
		SÜDSTRASSE 7	D-29348 ESCHADE	GERMANY
<p>I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.</p>				
SIGNATURE OF INVENTOR 203		SIGNATURE OF INVENTOR 204		
DATE		DATE		

24.07.01 *Ch. Bonemps*

9.07.01 *A. E. Chel...*